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Sublimation

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Introduction

Sublimation is not a procedure that is generally regarded as an analytical technique. It is a process, however, by which compounds can be purified or mixtures separated and as such can be of value as a single step or as an integral part of a more complex analytical method. It is applicable to a range of solids of inorganic or organic origin in a variety of different matrices and can be particularly useful when heat-labile materials are involved.

As a method of sample purification sublimation has been used to produce high-purity materials as analytical standards. A specific and common example of sublimation used as a means of purification is the removal of water from heat-labile materials in the process known as freeze-drying. The technique is described more fully below.

As a separation technique fractional sublimation has been used either to purify samples for analysis by removing undesirable components of the matrix or to remove the analyte from the matrix for subsequent analysis.

Principles

Sublimation is the direct conversion of a solid to a gas or vapour:

$$\text{solid} + \text{heat} \Rightarrow \text{gas or vapour} \quad (\text{heat} = \Delta H_{\text{subl}})$$

The heat supplied in this endothermic process is termed the heat of sublimation (ΔH_{subl}). The conditions under which sublimation occurs may be predicted for a given substance from its phase diagram, but in practice it is more common to use typical experimental parameters to determine the optimized procedure.

The heat of sublimation is a crucial parameter in deciding upon the applicability of sublimation to a particular substance, or indeed on the possibility of separating two components in a mixture.

An empirical approach to determining the appropriate temperature and pressure for sublimation can be used based upon previously determined data. The temperature (T, °K) and pressure (P) of sublimation can be related by an expression of the form:

$$\log_{10} P\,(\text{mmHg}) = A - (B/T)$$

in which the constants A and B for compounds of interest are available from published tables. The

result of the sublimation process can be seen in a freezer where ice sublimes and resolidifies as crystals. Iodine is a common substance that sublimes at room temperature and pressure; the result of this can be observed in a reagent bottle of the element.

The theory and mechanism of sublimation is of less practical importance to analytical procedures than it is in some other specialized areas of chemical science. Knowledge of sublimation characteristics can aid improvements in the stability of materials used at high temperatures or low pressures. For analytical purposes it should be sufficient to recognize that rates of sublimation depend upon the topology of the vaporizing surface (dislocations, atomic steps and ledge concentrations) and upon any atomic rearrangement that occurs during the sublimation process.

Experimentally, to effect sublimation, a number of criteria need to be satisfied. Firstly, the sample in question must be maintained at a temperature that ensures a sufficiently high vapour pressure for sublimation to occur, whilst remaining below that point at which the material either decomposes or melts. Secondly, a secondary surface must be available on which the sublimed vapour can condense or solidify. A number of experimental arrangements have been used that allow these criteria to be established; these are described in a later section of this article. It is also possible to enhance the sublimation process by changing the physical parameters under which the process is carried out:

- The sample may be heated in order to increase its vapour pressure.
- The application of a vacuum to the apparatus encourages vaporization and enhances the sublimation.
- Selectively cooling part of the apparatus increases the efficiency of the condensation process.
- Using an entraining gas can improve the mass transport in the system and thereby increase the overall efficiency of the sublimation process.

Apparatus

The simplest form of sublimation apparatus consists of a beaker or porcelain dish on top of which is placed an upturned watch-glass. The beaker contains the solid to be sublimed and the underside of the watch-glass provides the surface upon which the sublimed components condense (**Figure 1**). A perforated filter paper is commonly placed between the beaker and the watch-glass to prevent sublimate falling back into the sample.

A variant upon the above system uses an upturned funnel instead of a watch-glass as the condensing surface and an appropriately placed sealing ring improves the performance (**Figure 2**). Coils through which coolant is circulated can promote the sublimation process.

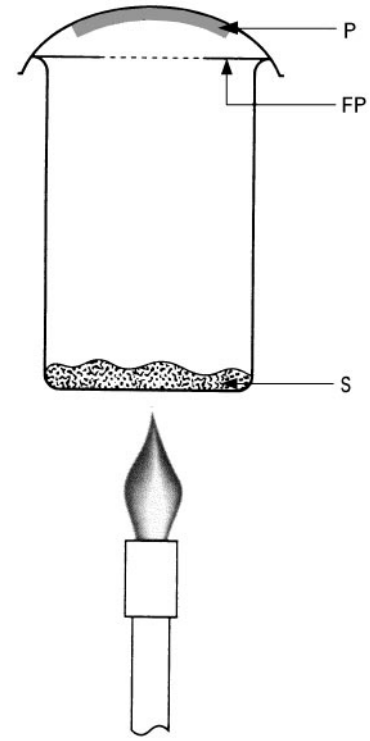

Figure 1 Simple apparatus for demonstrating the principles of sublimation. S, sample; P, sublimate (product); FP, perforated filter paper.

An early form of sublimation apparatus of which the above arrangements are derivatives (**Figure 3**)

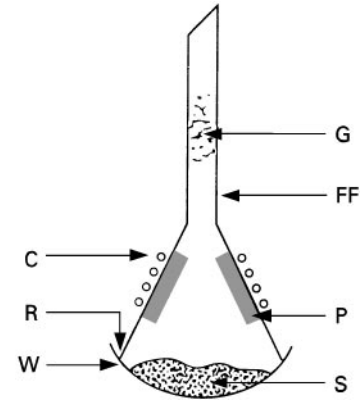

Figure 2 Apparatus for simple sublimation at atmospheric pressures. Watch-glass, W, with sample, S, surmounted by filter funnel, FF, with cooling coils, C, glass wool, G, and collected sublimed product, P. A sealing ring, R, is included between the watch-glass and filter funnel.

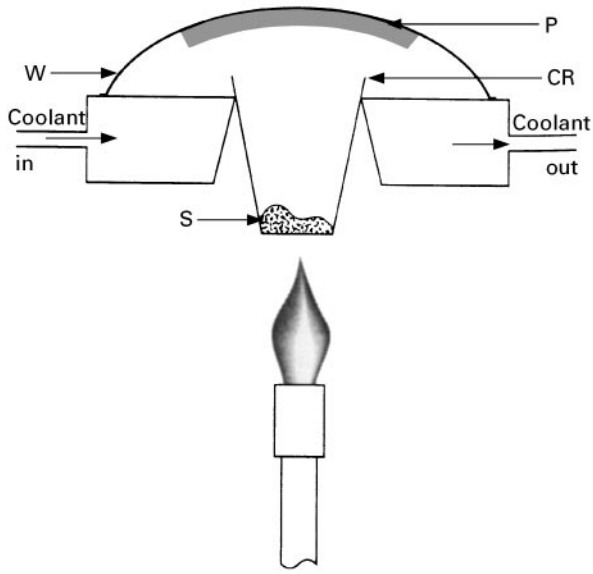

Figure 3 Early form of sublimation apparatus. The heated crucible, CR, rests in the cooling device. The sublimate product, P, collects on the underside of the watch-glass, W. S, sample.

included a means of cooling the surface on which the sublimate condenses. Cooling can be achieved in a number of ways, for example, using filter papers moistened with cool water, or in the case of the upturned funnel, a suitably shaped coil of circulating coolant liquid can be placed around the surface.

Sublimation under reduced pressure uses a modified form of apparatus in which a sealed enclosure allows a vacuum to be applied. The cooled surface is orientated with respect to the sample so as to maximize the condensation once sublimation has occurred (**Figure 4**). Reducing the distance that the sublimed substance(s) must travel is beneficial provided the necessary temperature gradient between sample and condensing surface can be maintained. An alternative arrangement for sublimation applications is shown in **Figure 5**.

Freeze-drying, a special application of the sublimation principle, uses apparatus of a different kind (**Figure 6**). The sample is dispersed around the walls of a round-bottomed flask whilst it is frozen by immersion in a suitable freezing mixture, for example dry ice–acetone. The flask is then attached to the evacuating system which usually comprises an oil vacuum pump protected from the ice sublimate by a train of condenser traps. Over a period of typically several hours the ice sublimes from the sample and condenses in the traps. Air is then admitted to the apparatus and the dried sample can be removed whilst the sublimed ice is drained off as water through the drain tap. Frequently this system is used to dry heat-sensitive materials such as enzymes and the process has been termed lyophilization.

Sublimation of metallic elements from rock or ore samples requires high temperatures. The equipment used is based upon silica furnace tubes in order to withstand the necessary conditions. The silica tube is heated in a furnace and the sublimate condenses either on a cool part of the tube or on a cooled surface immediately after leaving the tube.

The conditions of sublimation must be chosen according to the requirements of the application. For simple purification the sample temperature is raised slowly, under reduced pressure if necessary, until sublimate is observed on the condensing surface. These established conditions should then be maintained until no further sublimation appears to be occurring, at which point the sample temperature can be raised again if other components of the sample can be further removed. At any point in this cycle the apparatus can be dismantled and the sublimate removed. This process allows selective separation or fractional sublimation to be carried out.

Applications

Sublimation is applicable to a wide range of organic and inorganic compounds in an equally wide range

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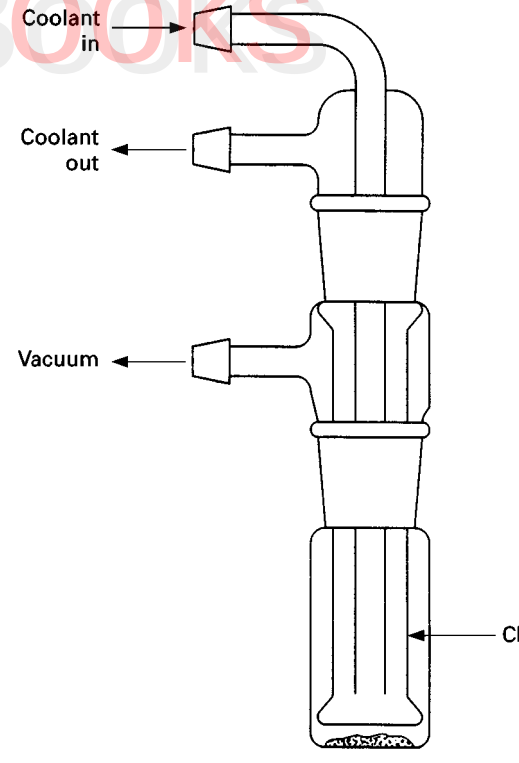

Figure 4 Apparatus for sublimation at reduced pressure. Coolant is circulated through the cold finger, CF, whilst a vacuum is applied to the sample chamber.

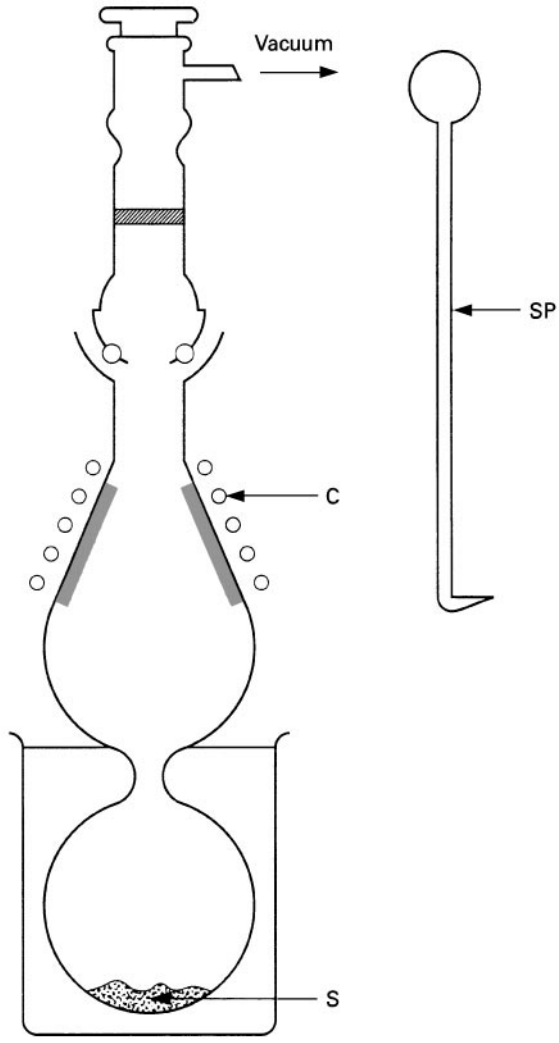

Figure 5 Improved sublimation apparatus proposed by Eisenbraun *et al.* (1978). Sample, S, sublimes from the lower to the upper chamber where condensation takes place on the cooled surface. A vacuum is applied to the apparatus and cooling coils, C, improve the condensation process. A specially formed spatula, SP, can be used to help remove the sublimate after the upper part of the apparatus is removed.

of different matrices. Sublimable substances include ice, iodine, arsenic(III) oxide, cadmium sulfide, ammonium chloride and a large number of organic compounds. Common matrices from which substances are sublimed include biological fluids, plant materials, carbonaceous materials, samples of crude organic solids and samples of rocks and ores.

Sublimation as a method of applying substances to thin-layer chromatography (TLC) plates involves the sample being sublimed and the vapour produced being directed by means of a drawn capillary onto the surface of a TLC plate which is slowly moved in one dimension. This results in the sublimed materials being deposited upon the TLC plate in a differential mode – the most easily sublimed compounds are deposited first whilst those requiring a higher temperature are deposited later. The TLC plate is then developed in the normal way to give what has been termed a 'thermofractogram' in which the substances are separated as a function of their heats of sublimation along one axis and as a function of their chromatographic characteristics along the other axis. This approach has been applied to a wide range of substances including pharmaceutical preparations, plant components and foodstuffs.

Only a very limited number of standard methods have been reported in which sublimation is an important aspect. These comprise an ASTM standard for measurement of sublimation from thermionic emitters, and two standards from Germany and Japan testing the stability of dyes and printing inks to sublimation. The first covers the determination of the quantity, rate, and identity of sublimed, evaporated, or sputtered materials, whilst the latter two are concerned with textile materials and semi-manufactured products.

Sublimation is often the mechanism by which preconcentration of an analyte is effected, although this fact is frequently not appreciated. Dynamic headspace concentration from solid samples such as plant materials, foodstuffs or polymeric materials occurs by sublimation of the volatile components. Indeed, given appropriate apparatus that can be operated at different temperatures for dynamic

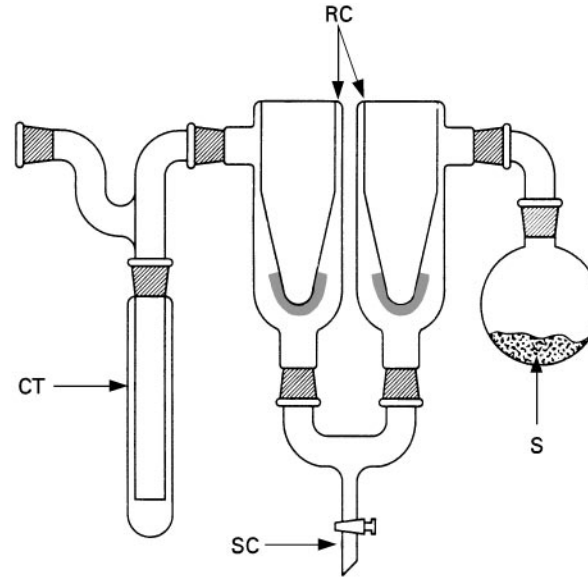

Figure 6 Typical freeze-drying apparatus. The frozen sample, S, is attached to the condenser assembly and a vacuum is applied. A cold trap, CT, protects the pump as ice sublimes from the sample and subsequently condenses in the refrigerant condensers, RC. On completion of the drying the sample is removed and the collected ice melts and drains from the system through the stopcock, SC.

headspace concentration, the heat of sublimation can be determined for various compounds.

Derivatization procedures carried out on crude samples can produce materials with improved sublimation characteristics. This technique has been used to produce volatile compounds of lanthanides and actinides which have then been sublimed prior to analytical determinations. Derivatives have been made using β-diketones (hexafluoroacetylacetone or acetylacetone), benzoyltrifluoroacetone and thenoyltrifluoroacetonates.

Low-temperature sublimation, which in some circumstances is termed freeze-drying, has been used to separate water, as ice, from biological fluids such as serum, urine or saliva. The technique has been particularly useful in paediatric cases where sample volumes are extremely low. Determinations have then been accomplished using IR spectroscopy or mass spectrometry. Preparation of physiological samples for determination of deuterium oxide has included sublimation techniques prior to spectrophotometric determinations.

Low-temperature sublimation has been used to prepare samples for cryo-scanning electron microscopy (SEM) analysis in order to examine herbicide particles in a water suspension. The sublimation of herbicide-containing frozen water droplets provides a suitable etching of the surface for the SEM technique.

High-temperature sublimations are often the methods of choice in sample preparations from mineral ores, particularly in the case of trace enrichment of noble metals and the actinides and lanthanides prior to activation methods. Temperatures of 800–1200°C are typical. The procedure is carried out in silica tubes with entrainment gases, for example air or argon, being used to increase the sublimation process.

Polycyclic aromatic compounds have been separated using sublimation techniques from a variety of samples including coal, solids derived from oil, coal and petroleum processing, and residues (soots) resulting from the use of such fossil fuels.

A variety of miscellaneous applications have been developed for separation from difficult matrices and purification of specific materials. These include:

- Mercury separated from impurities by conversion to its iodide followed by sublimation.
- Isolation of proazulene and chamomile from the flower heads of plants.
- Isolation of aroma compounds from wheat and rye samples prior to determination using isotope dilution methods.
- Determination of tin in casserite.
- Selective sublimation of molybdenum and tungsten.

Sublimation is used in some procedures for the preparation of samples for SEM in which gold is sublimed in vacuum from a heated tungsten filament to the sample being examined.

See also: **II/Distillation:** Freeze-Drying.

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Theory of Distillation

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Introduction

Distillation is a very old separation technology for separating liquid mixtures that can be traced back to the chemists in Alexandria in the first century AD. Today distillation is the most important industrial separation technology. It is particularly well suited for high purity separations since any degree of separation can be obtained with a fixed energy consumption by increasing the number of equilibrium stages.

To describe the degree of separation between two components in a column or in a column section, we